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FULL PAPER

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Hybridization of Al_2O_3 microspheres and acrylic ester resins as a synergistic absorbent for selective oil and organic solvent absorption

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In this study, we have focused on the synthesis, characterization, and oil absorption properties of Al_2O_3 microspheres/acrylic ester resin (AER) hybrids. The Al_2O_3 microspheres are prepared by a combined hydrothermal and sintering processes, followed by surface modification with silane coupling agent (KH 570). The Al_2O_3 microspheres/AER hybrids with a rough surface are synthesized by a microwave polymerization route by using modified Al_2O_3 microspheres as modifiers. In this hybrid materials system, the Al_2O_3 microspheres with porous structures may provide fast oil absorption due to the low oils absorption energy and short diffusion lengths. The resin hybrids exhibited reversible oils and organic solvents adsorption with maximum absorption capacities up to 29.85 g/g. This study suggests potential environmental advantage in using metal oxide microspheres in improving the oil absorption properties of oil-absorbing resins as absorbents for recovering oil and organic solvent from water.

KEYWORDS

absorption, acrylic ester resin, hollow microspheres, resin hybrids, reusability

1 | INTRODUCTION

As a nonrenewable resource, crude oil is an essential raw material for chemical industry and materials engineering. The worldwide consumption of crude oil for 2016 is predicted to be ~94 million barrels per day.[1] Crude oil exploration, storage, transportation, processing and usage activities are all accompanied by the risk of oil spillage.[2] Water pollution from oil spills has become one of the major threats to the environment and has become a global concern due to its toxicity and non-biodegradable properties. A typical example is the 2010 Gulf of Mexico oil spill, the largest accidental ocean spill in history, which released an estimated 4.9 million barrels of crude oil into the ocean,[3] resulting in severe damage to marine life, fishing industry, coastal wetlands and so on. Therefore, it is essential to separate and clean the oil promptly after a spillage.

Organic solvents, which are widely used in laboratory and industrial production, can release toxic organic pollutants into environment and thereby cause environmental contamination as well as resource and economic losses. The trace water organic solvents need to be removed before use.[4] The long-term effects of environmental pollution by oil spills or organic solvents/water separation call for an urgent need to develop separation technologies and relevant oil/water separation materials for the cleanup of oils and organic solvents from water.[5] Selective removal and separation of oils and organic solvents from water surfaces or under water by oil/water separating materials is of great interest from economic and ecological standpoints. Therefore, various oil-separating materials have been applied for separation of oils and organic solvents.

The preferable oil-separating materials should possess these properties such as high oil separation properties,[6] fast oil separation rate,[7] good reusability,[8,9] good mechanical and chemical stability.[10] In recent years, porous functional materials are interesting because of their wide range of applications, such as chemical separation and purification,[11,12] adsorption,[13,14] catalysis,[15] filtration[16] and drug delivery.[17] Utilizing the porous structures of foam material, Chen *et al.*[18] prepared porous carbon foam for selectively oils absorption via carbonization of polymer foam and reported the oils and organic solvents absorption capacity of 148.4-411.2 g/g. Dutta *et al.*[19] synthesized cone-shaped superhydrophobic CaAl-LDH intercalated with dodecyl sulphate anions that can separate and regenerate oil from oil–water mixtures. Among the porous materials, porous oxides are crucial because of their large surface area, lightweight and tunable surface properties.[20,21] In oils and organic solvents absorption, the large surface area of porous microspheres can effectively reduce the mass transfer resistance, resulting in fast sorption kinetics. In addition, the porous architectures of the microspheres can provide more space and absorption sites for oils and organic solvents absorption. Therefore, the development of porous oxide microspheres is of great significance in oils and organic solvents separation.

The oil absorption properties are limited by the pore structure and density of absorbents. As a novel class of functional polymer, oil-absorbing resins with 3D network structure, hydrophobic and oleophilic nature are considered as promising materials for oils separation due to the high oil retention ability, high selectivity and good reusability.[22–24] Nevertheless, low oil absorption properties, complicated fabrication procedures and poor thermal stability of oil-absorbing resins seriously hinder the practical applications in oil separation. To overcome these restrictions, introducing the porous functional materials into oil-absorbing resins was suggested. Wu *et al.*[25] prepared the magnetic, durable, superhydrophobic and superoleophilic polyurethane (PU) sponges by chemical vapor deposition of tetraethoxysilane to bind the Fe_3O_4 particles tightly on PU sponge surfaces. The Fe_3O_4/sponges also show very high efficiency in oil/water separation, which could absorb a large amount of floating oils on a water surface and heavy oils under water. Our group recently reported a facile and inexpensive to fabricate MnO_2 nanowires/PU foam composites,[26] using the MnO_2 nanowires as modifiers and PU sponge as a porous substrate. The obtained PU foam composites are demonstrated to have excellent oils absorption properties by introducing the MnO_2 nanowires and may have some promising applications in oils and organic solvents separation. However, the MnO_2 nanowires cannot provide enough oil storage space, and thus largely restricts the oils absorbency of the oil-absorbing resins.

Herein, to explore the advantage of porous oils absorption materials and oil-absorbing resins in terms of synergistic absorption, we report the synthesis and characterization of porous Al_2O_3 microspheres/AER hybrids. Furthermore, the prepared resin hybrids are employed for oils and organic solvents adsorption. Firstly, the Al_2O_3 microspheres were prepared by a simple hydrothermal method followed by calcination. Then, the porous Al_2O_3 microspheres/AER hybrids were synthesized by suspension polymerization. The introduction of porous Al_2O_3 microspheres into oil-absorbing resins can effectively improve the pore structure and stability of the resin hybrids, and thus improved the oils absorption properties. In order to explore the feasibility of resin hybrids as an absorbent, the oils absorption performances were evaluated using various oils and organic solvents. It is expected that the resin hybrids would have excellent oils absorption properties due to synergistic advantages of the high porosity of Al_2O_3 microspheres and swelling properties of resin, as well as the strong oils and organic solvents affinity attributable to the hydrophobic surface. It makes them very promising materials as an oil/water separator and oil absorbent.

2 | MATERIALS AND METHODS

2.1 | Chemicals and materials

N,N-methylene-bis-acrylamide (MBA), methyl methacrylate (MMA), polyvinyl alcohol (PVA), butyl acrylate (BA), γ-methacryloxypropyl trimethoxysilane (KH-570), benzoyl peroxide (BPO), ethyl acetate, polydimethylsiloxane (PDMS), toluene and carbon tetrachloride (CCl_4) and chloroform ($CHCl_3$) were obtained from Sinopharm Chemical Reagent Co., Ltd. Aluminum nitrate nonahydrate ($Al(NO_3)_3•9H_2O$) and glucose ($C_6H_{12}O_6$) were provided by Shanghai Chemical Company. Diesel oil and engine oil were collected from the local service station. Some edible oils, including soybean oil, sesame oil and sunflower oil, were purchased from the local supermarket. And the initiator BPO was recrystallized before using and stored in an amber bottle. Double-distilled water was employed in all experiments.

2.2 | Preparation and surface hydrophobic modification of porous Al_2O_3 spheres

The preparation of porous Al_2O_3 spheres was carried out by classical template method with a modification.[27] In a typical preparation, 15 mmol of glucose and 3 mmol of $Al(NO_3)_3•9H_2O$ were dissolved in 60 ml of distilled water to form a mixed solution under vigorous stirring for 30 min. The mixed solution was placed in a 80 ml Teflon-lined stainless steel autoclave and maintained at 180 °C for 24 h. The black products were collected and washed with distilled water and anhydrous alcohol several times. Then, the products were dispersed in 100 ml of distilled water and treated under ultrasound for 30 min. After that, the obtained products were filtered and washed several times with distilled water, and dried in air at 80 °C. Finally, the samples were calcined at 600 °C in air for 4 h to obtain porous Al_2O_3 microspheres (as shown in Scheme 1).

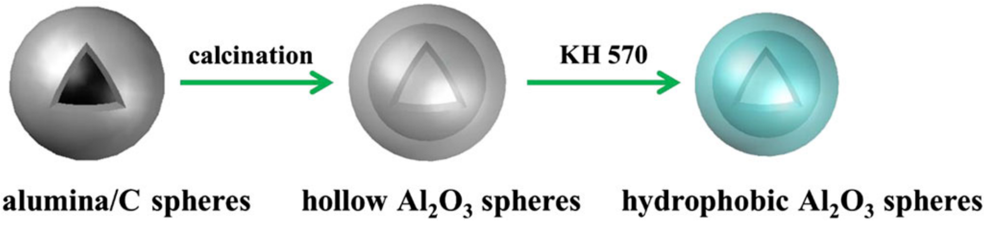
The hydrophobic modification of Al_2O_3 microspheres was performed by grafting the hydrophobic group on the surfaces of microspheres (as shown in Scheme 1). 50 mL of water suspension of porous Al_2O_3 microspheres (0.01 g/ml) was subjected to ultrasonic vibration for 20 min. The pH of the suspension was adjusted to 3-4 by careful addition of HCl (10 wt %). Then, 50 ml of anhydrous ethanol and 0.5 g of KH 570 were added into the mixture. The obtained mixture was sealed in a 250 ml three-necked round bottom flask and heated in a microwave reactor to 85 °C for 60 min, and the obtained powders were filtered, washed with distilled water, and then dried at 60 °C in air for 12 h before characterization.

2.3 | Synthesis of porous Al_2O_3 microspheres/AER hybrids

The porous Al_2O_3 spheres/AER hybrids were synthesized by utilizing the microwave polymerization between the grafted functional groups and monomer of AER on the porous spheres surfaces. Firstly, 0.27 g of PVA was dissolved in 27 ml of distilled water at 90 °C with a mechanical stirrer. After natural cooling, the PVA solution was transferred into a XH-100A microwave reactor. Then, the mixture, which contained hydrophobic porous Al_2O_3 spheres (0.27 g), BA (6.0 g), MMA (3.0 g), of ethyl acetate (4.5 g), BPO (0.09 g) and MBA (0.135 g), was added into the microwave reactor under N_2 atmosphere. The temperature was ramped from room temperature to preset reaction temperatures, and the reaction was continued at 40 °C for 15 min, 60 °C for 15 min, 80 °C for 150 min with stirring. After the reaction was complete, the product was collected and sequentially washed with deionized water (60~70 °C) and anhydrous ethanol, dried at 80 °C for 12 h to obtain porous Al_2O_3 spheres/AER hybrids.

2.4 | Sample characterization

The SEM images of the porous Al_2O_3 spheres, raw AER, and porous Al_2O_3 spheres/AER hybrids were acquired



SCHEME 1 Schematic illustration for preparation and surface hydrophobic modification of Al_2O_3 spheres

using a JEOL JSM- PLUS/LA scanning electron microscope. The surface properties and pore structures of as-prepared porous Al_2O_3 spheres were analyzed by nitrogen adsorption measurements, operated at 77 K on a Micromeritics ASAP 2020 adsorption analyzer. The contact angle of hydrophobic Al_2O_3 spheres was tested by using a commercial CAM200 optical system by the sessile drop method. X-ray diffraction (XRD) data were recorded using a Shimadzu XRD-6100 instrument with Cu Kα radiation at 40 kV and 30 mA, a scanning rate of 4°/min, and a 2 theta angle ranging from 10° to 80°.

2.5 | Oils adsorption

The oil absorption properties were evaluated by a weighing method via dipping resin hybrids into oils (or organic solvents)/water mixtures. In a typical absorption process, 0.2 g of resin hybrids was immersed in oils (including edible oils, organic solvents and fuels) at 25 °C for 24 h. After that, the samples were taken out from the oil, drained for 3~5 min to remove residual oil, and then weighed immediately. The oil absorption properties of resin hybrids were calculated by the following formula:

$$Q(g/g) = (m_t - m_0)/m_0 \tag{1}$$

where m_t and m_0 are the weight of the oil absorbents dispersed in oil for time t and the dry weight of the oil absorbent, respectively.

To test the regeneration capacity of the porous Al_2O_3 spheres/AER hybrids, the saturated organic solvents and oils were firstly squeezed from the oil-absorbing materials by a simple mechanical compression method. Then, the samples were immersed in anhydrous ethanol to release the absorbed oil, followed by drying at 120 °C for 12 h. The oils absorption and desorption process were repeated 5 times to confirm the reusability of resin hybrids. For each cycle, the resin hybrids were weighed before and after oils absorption.

3 | RESULTS AND DISCUSSION

As a carbon precursor, the glucose was hydrolyzed during the hydrothermal process, forming the carbon microspheres via the condensation, polymerization and aromatization of glucose. During this process, the alumina precursors are easily adsorbed to the surface of carbon spheres due to the oxygencontaining groups in the carbon spheres, forming the alumina/carbon spheres with a polycrystalline Al_2O_3 shell structure. Therefore, the porous Al_2O_3 microspheres are obtained by the calcination of the carbon spheres. Figure 1 shows the typical SEM images of alumina/carbon spheres and porous Al_2O_3 microspheres. As shown in Figure 1(a) and (b), the alumina/carbon particles are spherical in shape and relatively homogeneous. The microspheres shown in Figure 1B have a narrow particle size distribution with the mean size of 2.0 μm. Figure 1(c) and (d) give the SEM images of the porous Al_2O_3 microspheres. Observed from the images, it is obvious that the spherical morphologies are retained in Al_2O_3 microspheres. It is also noted that a rough surface is obtained after the thermal decomposition of the carbon

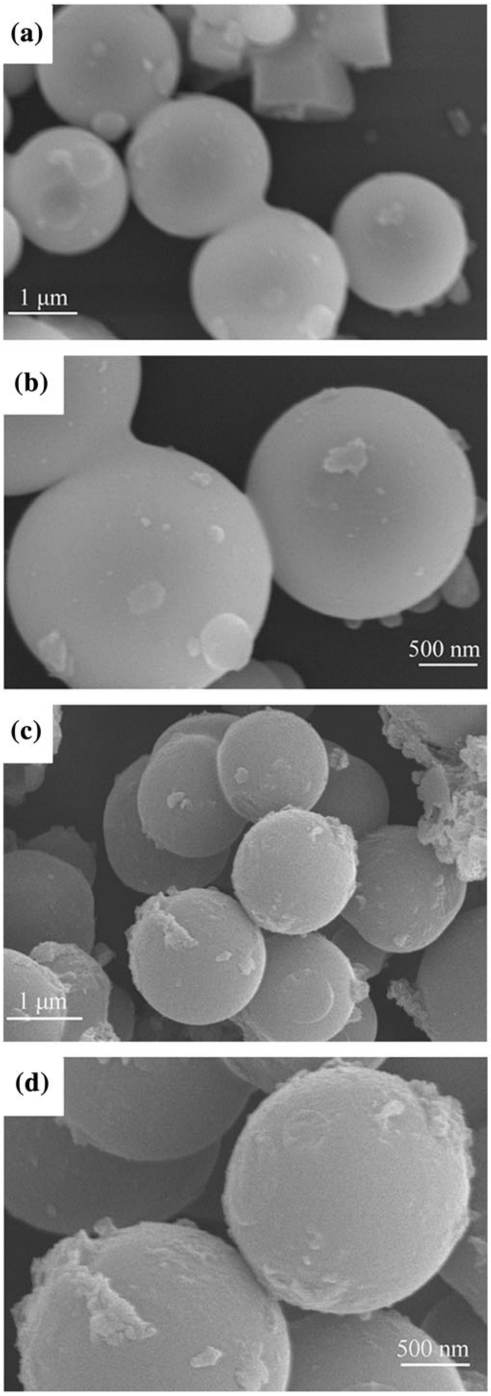


FIGURE 1 SEM micrographs of alumina/carbon spheres and hollow Al_2O_3 microspheres

spheres as revealed in Figure 1(d). They appeared to have rough surfaces, which is attributed to the fact that the amorphous Al_2O_3 is formed by the calcination.

In oils absorption, the large surface area of microspheres can effectively reduce the mass transfer resistance and rapid absorb organics from water. While, the porous structures of the microspheres can absorb oils, and store in the internal space of Al_2O_3. To obtain further insight into the surface properties of the as-prepared Al_2O_3 microspheres. The N_2 adsorption-desorption method was also employed to confirm the specific surface area and the pore sizes distribution of the obtained Al_2O_3 microspheres. Figure 2(a) shows their adsorption and desorption isotherm curve. The isotherm curve of Al_2O_3 microspheres exhibits the typical adsorption hysteresis that belongs to type IV isotherm curves, indicating that these the samples have mesoporous structures. The specific surface area and pore volume of samples are calculated to be 111.73 m^2/g and 0.1634 cm^3/g, respectively. The high BET surface area and mesoporous structures of the porous Al_2O_3 microspheres are beneficial to oils and organic solvents transport and absorption. A plot of the pore size distribution, calculated using the BJH method from the adsorption branch, is shown in the Figure 2(b).

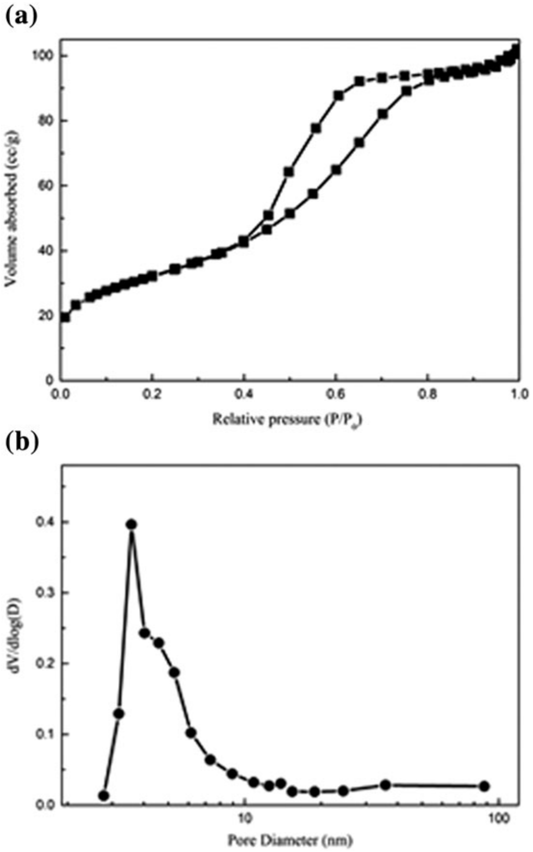


FIGURE 2 N_2 adsorption–desorption isotherm and BJH pore size distribution of hollow Al_2O_3 microspheres

It is seen from the pore sizes of porous Al_2O_3 microspheres are distributed mostly between 2.76 and 10.77 nm, a narrow pore size distribution centered at 3.55 nm, implying that the sample possesses uniform pore channels in the mesoporous region. The mesopores resulted in a higher surface area, which will facilitate the mass transfer from the liquid phase into solid phase.

For oils and organics selective separation, the surfaces modified Al_2O_3 microspheres, which are treated by surface grafting of hydrophobic groups, is suitable for the demand of interfacial hydrophobicity and lipophilicity. In addition, the grafted functional group can be related with the monomers of AER to form the organic-inorganic hybrids. Figure 3 presents the XRD patterns of porous Al_2O_3 microspheres and surface modified Al_2O_3 microspheres. In XRD patterns, the porous Al_2O_3 microspheres show showed only very broad and diffuse patterns, indicating the amorphous nature of the Al_2O_3 microspheres obtained by sacrificial template method. To further confirm the structural changes, the as-prepared Al_2O_3 microspheres were modified by hydrophobic functional groups and the corresponding XRD patterns are presented in Figure 3b. As can be seen in XRD pattern, no observable change in the Al_2O_3 microspheres was observed after surface hydrophobic modification, which meant that the silane coupling agent did not affect the structure of Al_2O_3.

In this case, the surfaces of porous Al_2O_3 microspheres were chemically modified using KH 570 in order to terminate the hydrophilic groups such as hydroxyl groups, forming the hydrophobic interface. In order to verify the changes on the surface properties of the Al_2O_3 microspheres, the surface functional groups of raw Al_2O_3 microspheres and surface modified Al_2O_3 microspheres were investigated by FT-IR spectroscopy. The broad

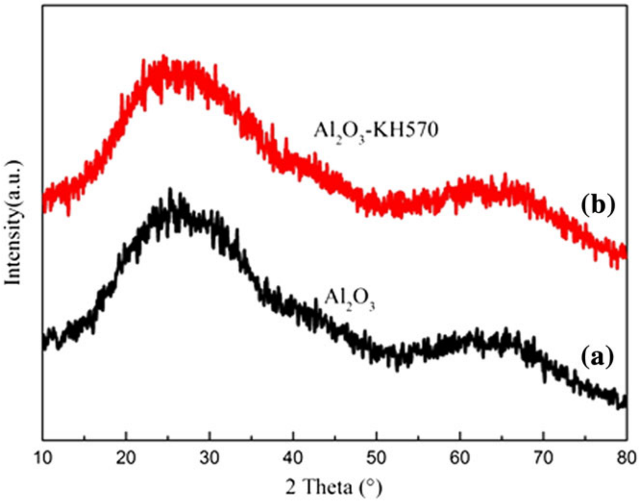


FIGURE 3 XRD patterns of raw and surface modified hollow Al_2O_3 microspheres

adsorption band at 3400 cm^{-1} could be ascribed to stretching vibrations of hydroxyl group. It can be seen from Figure 4a, the strong peaks at low frequency (880~530 cm^{-1}) in both spectra of raw Al_2O_3 microspheres and surface modified Al_2O_3 microspheres are attributed to the M-O vibration of chemical bonds in Al_2O_3. After surface modification of Al_2O_3 microspheres, a variety of surface functional groups were introduced onto the surface, as can be seen in Figure 4b. These functional groups centered at 2955.95 1704.45, 1635.75, and 1300.41 cm^{-1} could be ascribed to C-H, C=O, C=C, and C-O, respectively, indicating the existence of hydrophobic functional groups on the surface of Al_2O_3 microspheres. These results indicated that the hydrophobic groups are successfully grafted on the surfaces of Al_2O_3 microspheres. The surfaces of Al_2O_3 microspheres are treated by KH 570, resulting in the formation of hydrophobic interface. For comparison, the FT-IR spectrum of silane coupling agent is also given, as shown in Figure 4c. It should be noted that the peak intensities of surface modified Al_2O_3 microspheres are lower than that of pure silane coupling agent. The reason for this phenomenon may be due to the low content of hydrophobic groups in the Al_2O_3 microspheres.

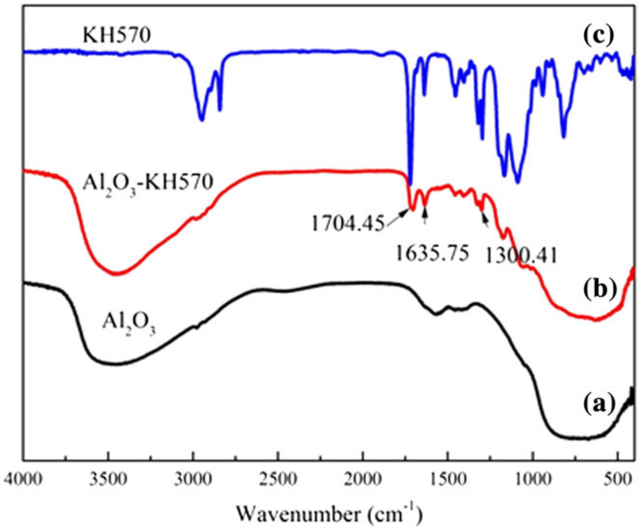


FIGURE 4 FT-IR spectra of raw hollow Al_2O_3 microspheres (a), surface modified hollow Al_2O_3 microspheres (b) and KH 570 (c)

Wettability of porous Al_2O_3 microspheres to water is one of the most important considerations when selecting an absorbent suitable for oils and organic solvents absorption. The surfaces of porous Al_2O_3 microspheres were chemically modified using KH 570 to form the hydrophobic interfaces. To further verify the surface properties, contact angle measurements were conducted to examine the surface wettability at different places of the samples. Figure 5 shows the water contact angle profiles of the substrates coated with the porous Al_2O_3 microspheres before and after surface modification. As shown in Figure 5(a), the contact angle of unmodified Al_2O_3 microspheres could not be measured because it was extremely low, indicating the existence of lipophilic. When KH 570 coated on Al_2O_3 microspheres contacted with the oil-water mixture, oils molecules can be trapped in the macroporous structure of materials. It can be seen from Figure 5(b) and (c) that the droplets are nearly spherical in shape for surfaces modified Al_2O_3 microspheres. The water contact angle,

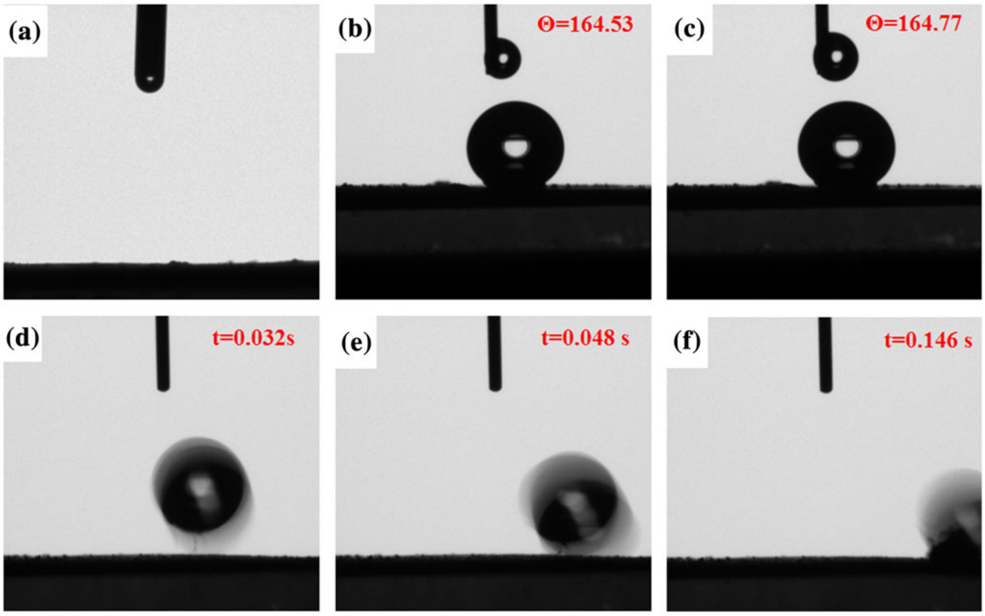
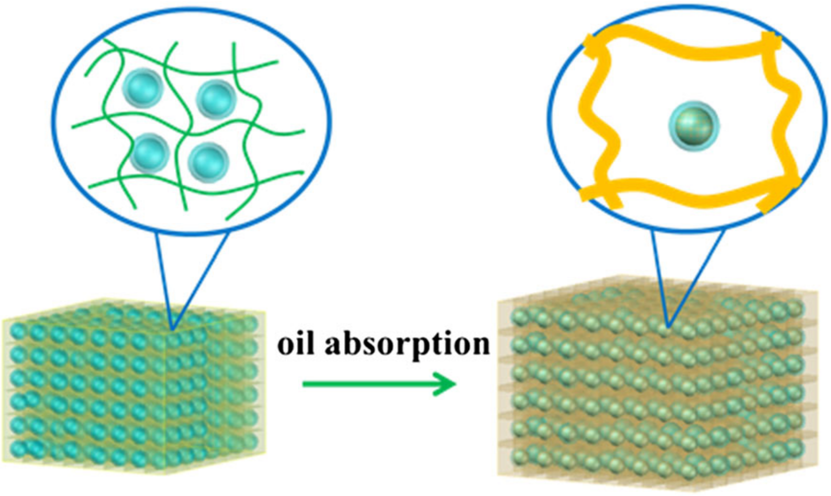


FIGURE 5 Oil (a) and water (b and c) wettability of the substrates coated with the KH 570 modified hollow Al_2O_3 microspheres; Water droplet rolling on the femtosecond laser ablated surface (e-f)



SCHEME 2 Schematic illustration for oils absorption of hollow Al_2O_3 microspheres/AER hybrids

measured at room temperature, was varied between 164.53° and 165.77°, implying that superhydrophobic properties of microspheres closer to the grafted hydrophobic functional groups. Besides, while immersing surfaces modified Al_2O_3 microspheres in aqueous solution for 6 h under the condition of ultrasonic vibrations or exposing samples in air environment for 5 days at room temperature, samples in both cases remained hydrophobicity with water contact angle higher than 160°. It is clearly indicated the high stability of the hydrophilic or lipophilic properties of surface hydrophobic modification of Al_2O_3 microspheres. Figure 5(d)-(f) displays the rolling process of a water droplet on the alumina coating surface. When the droplet was falling on the surfaces modified Al_2O_3 microspheres surface, it bounced immediately without any delay. In the case of an inclined surface, the water droplet rolled off the surface quite quickly within a very short time. The ultimate tilt angle of substrate when the droplet started to roll was below 2°. The results indicate that the hydrophobic groups are successfully grafted on the surfaces of Al_2O_3 microspheres, which are in agreement with the FT-IR results as shown in Figure 4.

For the oils and organic solvents absorption of organic-inorganic hybrid materials, the absorption properties of hybrid materials are largely determined by the pore structures (inorganic absorbing materials) or swelling properties (polymer absorbing material). The porous structures of oil-absorbing materials are beneficial for reducing the mass transfer resistance and accelerating the oil absorption rate. The swelling properties of oil-absorbing resins not only determine the oils absorption properties of obtaining materials (as shown in Scheme 2), but also affect the retention ability of materials. The morphologies of the raw AER and Al_2O_3 resin hybrids were observed by the SEM images displayed in Figure 6. It appears from the observation of the surfaces of raw AER that they have a smooth and dense surface appeared without apparent porosity. It made oil molecules and organic solvents not easy to diffuse into the interiors of AER. However, the surface structures of resin hybrids are changed greatly by adding the porous Al_2O_3 microspheres, which can be observed from Figure 6(c) and (d). The resin hybrids exhibited a convex surface, which are beneficial for organic molecules absorption and diffusion into the interiors of materials. In this hybrid materials system, the porous Al_2O_3 microspheres with hierarchical porous structures may provide fast oil absorption owing to the lowering of absorption energy and diffusion length. In addition, the porous structures of Al_2O_3 microspheres may provide more oil storage space that can enhance the oil absorption efficiency. Compared with the raw AR, thermal stability of resin hybrids is improved slightly enhanced by introducing inorganic materials (see Supporting Information).

With low density, high porosity, superhydrophobicity, and excellent flexibility, the as-prepared resin hybrids can be considered as ideal oil absorbents to separate oils and organic solvents from water. In order to investigate the absorption properties, the resin hybrids were immersed in oils or solvents without water and the maximum absorption capacities were determined by mass change. Several kinds of frequently encountered oils, namely PDMS, soybean oil, sesame oil, sunflower oil, engine oil, and castor oil, were used to evaluate the absorption properties of the resin hybrids, and the results are shown in Figure 7(a). The oils absorption capacities of the resin hybrids towards different organic solvents range from 1.88 g/g to 2.95 g/g, partly depending on the density, viscosity and surface tension of the solvents. The absorbed organics are stored in the 3D network structure of oil absorbing resins.

To further verify the feasibility for oil/water separation applications, the dyed edible oils were chosen as a model absorbate to investigate the separation performance of

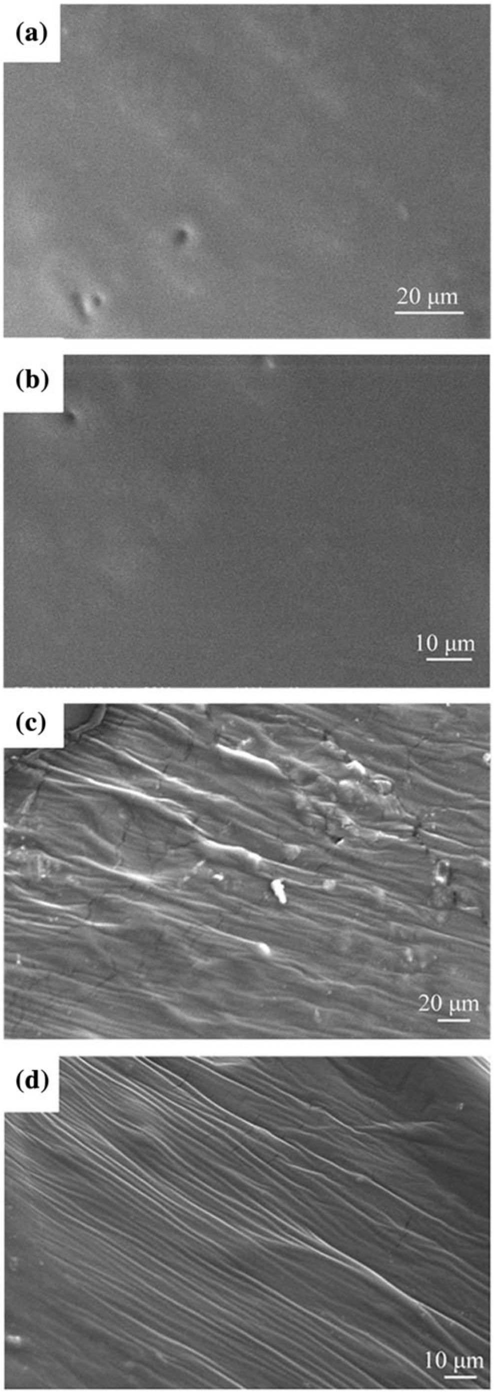


FIGURE 6 SEM images of raw AER (a and b) and hollow Al_2O_3microspheres/AER hybrids (c and d)

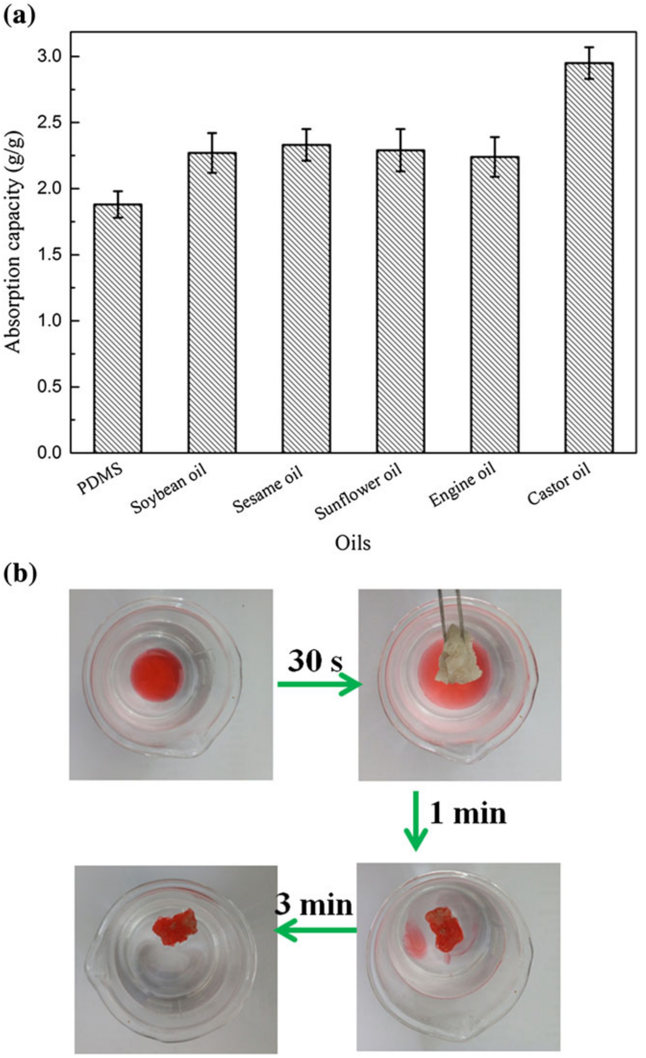


FIGURE 7 (a) Comparison of oils absorption capacities of resin hybrids, (b) photos of edible oils absorption from oily water by resin hybrids

the resin hybrids. As can be seen in Figure 7(b), when the resin hybrids were dropped on the oil/water surface, it absorbed the surrounding oil film at once. Thereupon, the white resin hybrids become succulent full with red oil within 3 min, resulting in transparent and clear water. Such rapid absorption process is due to the combined effect of its high porosity of porous Al_2O_3 microspheres and excellent swelling properties of oil-absorbing resins (as shown in Scheme 2). Owing to the oleophilic nature, it was able to be easily fetched out without assimilating any moisture.

The versatility of resin hybrid for the adsorption of organic compounds was also studied by employing a series of commonly used organic solvents, such as acetone, DFM, $CHCl_3$, ether, CCl_4 and THF. It can be seen in Figure 8(a) that the resin hybrid exhibited a very high absorption capacity (6.54 - 29.85 g/g). It was obvious that the resin hybrids reported here exhibited much higher adsorption capacity than oil-absorbing resins. To demonstrate the feasibility of heavy organic solvents absorption, chloroform dyed with Sudan III was selected as the representative absorbates on behalf of organic solvents for absorption. Compared with several reported oil-absorbing materials for oils and organic solvents absorption (Table 1), the hybrid resins show a high oil absorption capacity, and the maximum oil absorption capacity can reach up to 29.85 g/g. As can be seen in Figure 8(b), the resin hybrids

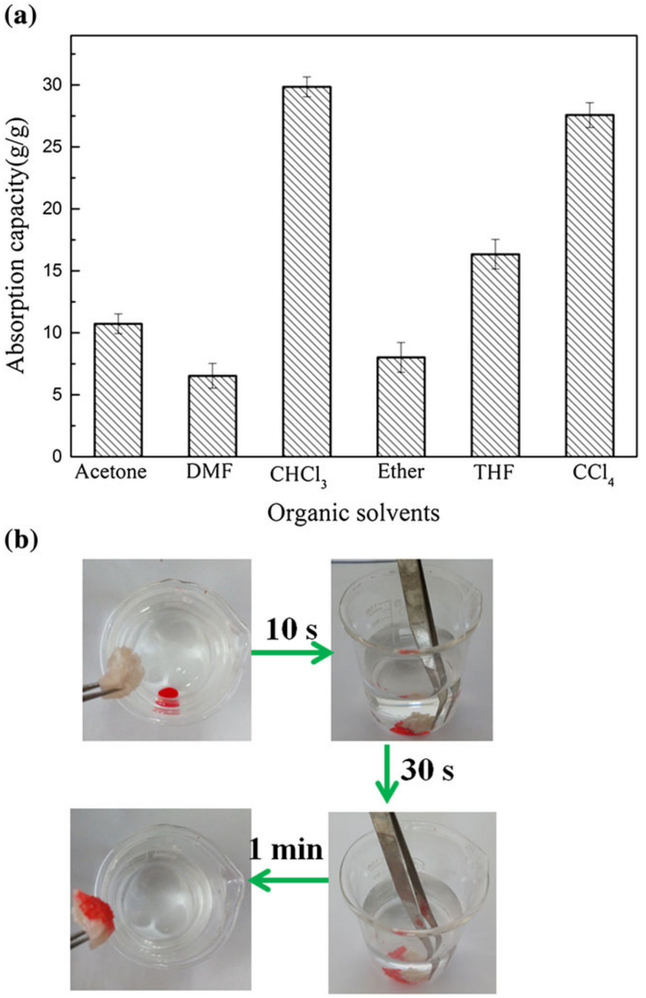


FIGURE 8 (a) Comparison of organic solvents absorption capacities of resin hybrids, (b) photos of chloroform absorption from oily water by resin hybrids

TABLE 1 Comparison of several reported absorbents for oils and organic solvents absorption

Adsorbents	Q (g g^{-1})	References
Cellulose/chitosan composite aerogel	10	[28]
SPION/b-cyclodextrin	7.2	[29]
Polymethacrylate-based Fiber	1.0-19.6	[30]
superhydrophobic sponge	25.0	[31]
Populus fiber	3.9-18.4	[32]
Ferric oxide nanoparticles doped carbon nanotubes	7.0	[1]
Pure oil absorption resins	23.5	[33]
Hybrid resins	6.54 - 29.85*	This work

could be also used for the absorption of heavy organic solvents under water. When the resin hybrids were immersed in the water, a silver mirror-like surface is observed owing to a continuous air layer trapped between the hybrids surface and water. The chloroform in contact with the resin hybrids is rapidly absorbed, and no obvious organic solvents remain in the water after taking the resin hybrids out. This commendable property indicated the possibility for environmental applications in absorbing floating pollutants and those underwater. Therefore, the resin hybrids were effective with low cost and high performance, environment-friendly and had a high scalability for the practical separation of oil/water mixture.

Effect of contact time on oils and organic solvents absorption is presented in Figure 9(a) and (b). It can be seen that the increase in the contact time led to an increase in oils and organic solvents absorption capacity. The oils adsorption was very fast in the first 60 min and after 80 min, complete oils and organic solvents absorption was obtained. In order to get further information on the oils and organic solvents absorption process, the oils adsorption obtained from different oils and organic solvents were further analyzed by different kinetic

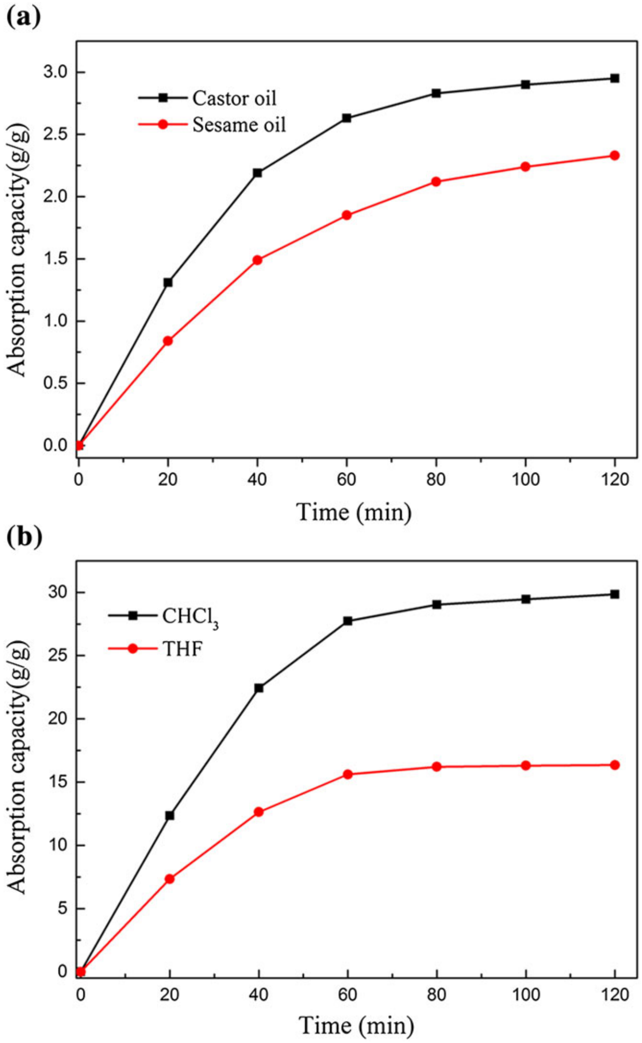


FIGURE 9 Effect of contact time on oils and organic solvents absorption

models (pseudo-first order equation, pseudo-second order equation and intraparticle diffusion). The kinetic models and correlation coefficients for oil and organic solvent absorption are compiled in Table S1. The sesame oil, $CHCl_3$ and THF adsorptions were fitted well by the pseudo-first order equation over the entire absorption process according to the high correlation coefficient (R^2>0.97). However, the intraparticle diffusion model fitted the castor oil adsorption very well according to the high correlation coefficients (R^2).

Reusability of oil-absorbents is a significant property for oil separation in practical application. As far as oil absorbency is concerned, the resin hybrids are also reusable, besides having excellent performance in oils and organic solvents absorption. During the cycled experiments, the as-synthesized resin hybrids were firstly immersed in oils and organic solvents for saturated absorption. After each absorption experiment, it was easy to clean resin hybrids by ethanol. 5 times cycled absorption experiments were performed and results were shown in Figure 10. It is worthy to note that no obviously measurable weight loss of the samples was detected after being reused, indicating that resin hybrids still displayed high oils absorption efficiency. The slightly reduced absorption properties can be ascribed to the fact that a handful of soluble fraction remained in the composites is dissolved in repeated swelling, and a fraction of network might collapse by extraction and drying.

As suggested by the results above, the as-prepared resin hybrids can be suitable for the separation of various types of oils and organic solvents with high oil separation properties, fast oil separation rate and good reusability. These could imply the resin hybrids as a good candidate for the cleaning up of oil-polluted water or water-polluted oil from both industrial drainage and daily emission.

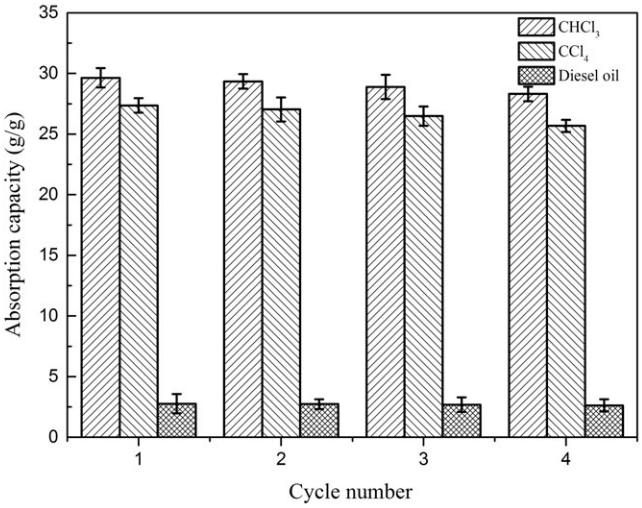


FIGURE 10 Absorption capacity of several oils for five absorption-regeneration cycles

4 | CONCLUSIONS

In summary, we have synthesized the porous Al_2O_3 microspheres/AER hybrids by a microwave polymerization route by using Al_2O_3 spheres as modifiers. The porous Al_2O_3 spheres were prepared by a combined hydrothermal and sintering method. In order to enhance the hydrophobicity and reactivity, the surfaces of Al_2O_3 spheres were chemically modified using silane coupling agent. The results demonstrated that all surface modified Al_2O_3 microspheres showed high water contact angles (>160°), implying that the hydrophobic groups are successfully grafted on the surfaces of Al_2O_3 microspheres. The large surface area of Al_2O_3 microspheres can effectively reduce the mass transfer resistance and rapid absorb organics from water. And the absorbed oil can be stored in the porous architectures of the microspheres. The as-prepared resin hybrids can separate the oil/water mixtures effectively with the maximum oil absorbency of high up to 29.85 g/g. Owing to their unique pore structures and superhydrophobic and swelling properties, the resin hybrids can absorb not only floating oil but also heavy organic solvents underwater with high selectivity and absorption capacity. Furthermore, the reusability studies confirm the repeatable usage of the resin hybrid and its efficacy in oil spill remediation. We believe that introduction of porous microspheres into oil-absorbing resins will widen the range of their applications in oily wastewater treatment, oils absorption and separation.

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SUPPORTING INFORMATION

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